ABSTRACT

Physico – chemical forces assumes great importance in understanding the behaviour of fine - grained soils As the soils become more and more finer, the dominance of these forces increases and may even control their behaviour totally This is because of the fact that the small soil particles are colloidal in nature with large specific surface area and charges on their particle surface The physical behaviour of such soils is explained using physico-chemical models and, as a result, estimation of surface potential and the variation of potential with distance become of paramount importance This thesis presents methods, which reduce the difficulties currently met with in obtaining mid - plane potential for different clay water electrolyte systems The most commonly acknowledged source of surface charge on soil colloids is from the structural imperfection in the interior of the crystal structure Structural imperfections, due to ion substitution or site vacancies, frequently result in permanent charge on the soil colloidal particle The charges on clay particles are usually negative and they repel each other in water There are exchangeable cations to satisfy the negative charges on clay particles These ions, which are close to the clay surface in the dry clay, start diffusing away from the surface of the clay particle in water Also the cations and anions present in the pore fluid are attracted or repelled by the negative charge on the clay surface The negative charge on the clay surface and the diffused ions in the pore fluid together is called diffused double layer The distance from the particle surface (measured in A^0) to the interface between the diffuse layer and equilibrium solution is called thickness of diffuse double layer The thickness of the diffuse double layer affects the fine - grained soil behaviour and structure For example, to predict the volume change behaviour of the soils, in general, research workers widely use "Gouy – Chapman theory" which is very well defined and used in colloidal chemistry Gouy-Chapman theory uses Poisson equation to determine the interfacial

potential and Boltzmann equation to describe the concentration profile in the diffuse layer around the platelet The diffuse double layer theory has been extended, by previous research workers, for the interacting diffused plates to model the volume change behaviour of clayey soils

In this work, an attempt has been made to relate the potentials of interacting and non – interacting plates of homo valent ionic system It is found that a relationship exists between the potential at any distance from the surface for non-interacting system, $\phi_{x=d}$, with the mid - plane potential of the interacting systems, ϕ_d in the form a fourth degree algebraic equation These relationships for mono and divalent ionic system are given separately in eqs (1) and (2) which are applicable for different electrolyte concentrations

for valence=1,

$$\phi_d = -8\times10^{-08}\phi^4_{@x=d} + 4\times10^{-05}\phi^3_{@x=d} - 9\,1\times10^{-03}\phi^2_{@x=d} + 1\,7622\phi_{@x=d} + 0\,9126 \quad (1)$$

for valence =2,

$$\phi_d = -5\times10^{-07}\phi^4_{@x=d} + 2\times10^{-04}\phi^3_{@x=d} - 1\,61\times10^{-02}\phi^2_{@x=d} + 1\,6999\phi_{@x=d} - 0\,0087 \quad (2)$$

Equations (1) and (2) are rearranged for the calculation of single plate potential from mid-plane potential of an interacting system are given in eqs (3) and (4)

for valence=1,

$$\phi_{@x=d} = 3\times10^{-8}\phi^4_d - 2\times10^{-5}\phi^3_d + 0\,0049\phi^2_d + 0\,4469\phi_d + 0\,0805 \quad (3)$$

for valence=2,

$$\phi_{@x=d} = 2\times10^{-07}\phi^4_d - 7\times^{-05}\phi^3_d + 0\,0088\phi^2_d + 0\,4887\phi_d + 0\,2563 \quad (4)$$

The repulsive pressure between the diffuse plates is a function of swell pressure of the soil mass and the distance between the diffuse plates is a function of void ratio Therefore, to establish a relation between the swell pressure and void ratio it is necessary to calculate the mid-plane potential in the diffuse part of the interacting ionic double layers The major difficulty in these calculations is the elliptic integral of first kind involved, which relates, half space distance and mid plane potential Several investigators circumvented this problem using indirect methods or by using cumbersome techniques

As, the calculation of potential at any distance from the surface in non – interacting system is quiet easy, the above equations are advantageously used and a simple procedure to find the potential – distance relationship in homo valent ionic system is proposed by eliminating the elliptic integral calculations The accuracy of the method has been checked by comparing the potential distance relationship with that obtained using the van Olphen procedure, which involves interpolation of data of two values of mid plane potential and slope of the curve near the surface with the use of tables The proposed method's accuracy depends on the coefficient of regression between the interacting and non - interacting curves, which are almost, equal to one On the other hand, in the van Olphen procedure, the accuracy depends on the interpolation of the data between the values of the slope of the surface potential, which may not vary linearly always The advantage of the proposed method is that there is no need to assume the variation between two values of mid plane potential and the slope of the curve near the surface

There exist very few methods to calculate potential – distance relationship in mixed ionic system, which is more general case of the soil – water – electrolyte system To find the potential – distance relationship in interacting mixed mono and divalent ionic systems, the existing methods involve, approximations or complications in the calculations of surface potential – mid-plane potential relationship and potential with distance from the surface of the plate These approximated equations, which work at very strong interactions of the diffuse plates, have been used by several research workers for obtaining potential-distance relationship for both strong and weak interactions of the clay platelets In this work, simple explicit equations relating surface potential and mid-plane potential are presented as the surface potential vary with the amount of interaction other than electrolyte and clay properties

$$\text{Surface potential } \Psi_s = \cosh^{-1}\left(\frac{-1\pm\sqrt{1+8\chi R+8R^2}}{4R}\right) \tag{5}$$

where, $\chi = \frac{\beta}{C_0} + \cosh u + R\cosh(2u)$ and $\beta = \frac{1000\pi\Gamma^2}{N\varepsilon KT}$

$$\text{Mid-plane potential } u = \cosh^{-1}\left(\frac{-1\pm\sqrt{1+8\delta R+8R^2}}{4R}\right) \tag{6}$$

where, $\delta = \cosh y_s + R\cosh(2y_s) - \frac{\beta}{C_0}$, R the ratio between the molar concentrations of divalent to mono valent cations, Γ_s is the surface charge density, N is the Avagadro's number, ε is the di – electric constant, K Boltzmann constant and T is the absolute temperature

Explicit integral equation given in (7) is derived for the estimation of mid-plane potential and half-space distance relationship in mixed mono-divalent ionic systems with and without the presence of anions in the equilibrium solution

$$d\sqrt{C_0} = 2.152\sqrt{R+1}\int_u^{y_s} \frac{dy}{\left[\begin{matrix}(\cosh y - \cosh u) + R(\cosh(2y) - \cosh(2u)) + \\ (1+2R)(\cosh(-y) - \cosh(-u))\end{matrix}\right]^{1/2}} \qquad (7)$$

Equation (7) is solved for different ratios of molar concentrations of divalent to monovalent ions $\left(R = C^{++}/C^{+}\right)$ by numerical method using "MATHEMATICA" tool The result is presented in the form of four axis plots showing the electrostatic potential (u and z) as a function of surface charge density, equilibrium solution concentration, and halfway distance between the plates These plots can be used for the estimation of potential – distance relationship for different electrolyte and clay properties for strong and small interaction of the plates as well The approximated equations, which have been used by the research workers, are compared with the result obtained from the exact equations, which are derived in this work The present approach is more universal applicability than the earlier methods, which are applicable only when the interactions between the diffused plates are very small or strong The influence of anions, present in the equilibrium solution, on the surface potential calculations and on potential – distance relationships has been studied and the results presented